

1-1-2005

Thermodynamics and Proton Transport in Nafion - I. Membrane Swelling, Sorption, and Ion-Exchange Equilibrium

P. Choi

N. H. Jalani

Ravindra Datta

Worcester Polytechnic Institute, rdatta@wpi.edu

Follow this and additional works at: <http://digitalcommons.wpi.edu/chemicalengineering-pubs>



Part of the [Chemical Engineering Commons](#)

Suggested Citation

Choi, P., Jalani, N. H., Datta, Ravindra (2005). Thermodynamics and Proton Transport in Nafion - I. Membrane Swelling, Sorption, and Ion-Exchange Equilibrium. *Journal of the Electrochemical Society*, 152(3), E84-E89.

Retrieved from: <http://digitalcommons.wpi.edu/chemicalengineering-pubs/27>

This Article is brought to you for free and open access by the Department of Chemical Engineering at DigitalCommons@WPI. It has been accepted for inclusion in Chemical Engineering Faculty Publications by an authorized administrator of DigitalCommons@WPI.



Thermodynamics and Proton Transport in Nafion

I. Membrane Swelling, Sorption, and Ion-Exchange Equilibrium

Pyoungho Choi,* Nikhil H. Jalani, and Ravindra Datta**z

Fuel Cell Center, Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts 01609, USA

A thermodynamic model is proposed to describe the sorption of water in Nafion based on the Flory-Huggins activity model and an appropriate osmotic pressure correction term for the chemical potential of water within the swollen membrane. The key variables for sorption are equivalent weight of ionomer, acid strength of the ionic groups, modulus of polymer elasticity, and interaction between water and polymer. The water uptake per unit mass of dry Nafion increases with the increasing acid strength of the functional groups, decreasing Young's modulus, and decreasing equivalent weight of Nafion. The model provides insights into the sorption and swelling behavior of ion-exchange membranes, and thus, may be useful in evaluating and designing alternate proton-exchange membranes for fuel cell applications. In a companion paper (Part II), a predictive model is presented for the transport of protons in Nafion.

© 2005 The Electrochemical Society. [DOI: 10.1149/1.1855872] All rights reserved.

Manuscript submitted February 23, 2004; revised manuscript received August 2, 2004. Available electronically January 24, 2005.

Fuel cells offer a palpable challenge to the conventional power-generating technologies due to their high efficiency, low environmental impact, and numerous potential applications.¹⁻³ The proton-exchange membrane (PEM) functions as a solid electrolyte in PEM fuel cells, conducting protons from anode to cathode as well as a separator for the reactant gases, protons, and electrons, thus, constitutes the heart of the PEM fuel cells. The most studied PEM is Nafion, consisting of a hydrophobic polytetrafluoroethylene backbone and a hydrophilic acid group $\text{SO}_3^- \text{H}^+$ connected to the backbone via side chains of $-\text{O}-\text{CF}_2-\text{CF}_2-\text{O}-\text{CF}_2-\text{CF}_2-$. Even though it is not cross-linked, Nafion is stable in the presence of water due to a balance of the hydrophobicity and hydrophilicity combined with its elastic strength, is chemically inert in both oxidative and reductive environments, and is an excellent proton conductor under typical fuel cell operating conditions. For its commercial application in fuel cells, however, it suffers from some drawbacks as well,³ e.g., a limitation in the operating temperature of around 80°C due to drying above 100°C in atmospheric fuel cells and softening over 111°C, as well as a high cost.

These limitations have stimulated a worldwide effort to find alternatives to Nafion, and a number of new membranes have been proposed, and discarded, based on their conductivity, cost, degradation, and stability (thermal, mechanical, and chemical). The PEMs are of essentially two types.⁴⁻⁶ (i) PEMs in which the acid site is covalently bound to the polymer and (ii) polymer composite membranes (PCMs) in which basic polymers are doped with other components such as acids and inorganics. PEMs are of the following types based on their chemical structure and resistance to degradation: (i) perfluorinated polymers, e.g., Nafion, Flemion, Gore-Select and Dow membranes; (ii) partially fluorinated polymers, e.g., poly- α,β,β -trifluorostyrene, and Ballard Advanced Materials 3rd Generations (BAM3G) polymers; and (iii) hydrocarbon polymers, e.g., poly(phenylene oxide) PPO, poly(ether ether ketone) PEEK, poly(phosphazene) PP, poly(imides) PI, and poly(benzimidazole) PBI. Examples of PCMs⁵ include sulfuric acid (or phosphoric acid) doped PEO (PEO/ H_2SO_4 or PEO/ H_3PO_4) and inorganic acid incorporated Nafion such as Nafion/ZrP (zirconium phosphate), and Nafion/PTA (phosphotungstic acid).

The proton conductivity of PEMs depends strongly on the host polymer structure and water content of the membrane.⁷ A central challenge in the rational design of new PEMs is thus a fundamental understanding of the structural and water uptake characteristics needed to achieve high proton conductivity. The proposed theoretic

cal structural models of Nafion include:⁸ Gierke's cluster-network model,⁹ Mauritz *et al.*'s elastic model,¹⁰ Yeager and Steck's three-region model,¹¹ and other more recent models based on the spectroscopic analysis such as SANS,¹² SAXS,¹³ and AFM.¹⁴

The water uptake by polymer membranes at a given relative humidity (RH) is a function of temperature,^{15,16} equivalent weight (EW),^{17,18} type of counterions,^{19,20} and membrane pretreatment.^{15,21} Although several empirical models of water uptake in Nafion have been proposed, e.g., based on a finite multilayer Brunauer-Emmett-Teller (BET),²² modified BET,²³ and Flory-Huggins,^{23,24} these models provide a limited theoretical understanding of sorption in PEMs. Recently, we have proposed²⁵ a more insightful thermodynamic model that incorporates the effect of swelling pressure within the membrane on the chemical potential of water and hence sorption, based on a "spring constant" of the polymer matrix used as a fitted parameter. Here we propose a more general version of our thermodynamic model²⁵ that involves the Flory-Huggins theory,²⁶ incorporating configurational (entropic) and interactive (enthalpic) contributions for activity, and uses the Young's modulus of membrane elasticity to obtain the osmotic pressure due to polymer stretching. In our previous model,²⁵ mole fraction was used simply for activity. Further, the interaction between the membrane and solvent was not explicitly accounted for but was incorporated within the spring constant κ . In the present work, the sorption of water in Nafion is analyzed and design parameters are deduced from this more fundamental model, which also contains the Flory-Huggins interaction parameter, accounting for the interaction between the polymer and water. The Young's modulus is measured here using the novel technique of optoelectronic holography (OEH), and the sorption from vapor phase is measured using the tapered element oscillating microbalance (TEOM) technique.

Theory

Thermodynamic equilibrium.—A generalized chemical potential $\mu_{i,\alpha}$ of species i in phase α can be written as a function of temperature T , pressure P , activity a_i , and other potentials Φ . Assuming these effects to be separable

$$\frac{\Delta\mu_{i,\alpha}}{RT} = \frac{\Delta\mu_{i,\alpha}(T)}{RT} + \frac{\Delta\mu_{i,\alpha}(P)}{RT} + \frac{\Delta\mu_{i,\alpha}(m)}{RT} + \frac{\Delta\mu_{i,\alpha}(\Phi)}{RT} + \dots \quad [1]$$

where $\Delta\mu_{i,\alpha}(m)$ contains the configurational (entropic) as well as interaction (enthalpic) terms of mixing. Thus

* Electrochemical Society Student Member.

** Electrochemical Society Active Member.

z E-mail: rdatta@wpi.edu

$$\mu_{i,\alpha} = \mu_i^\circ(T, P^\circ) + \int_{P^\circ}^P \bar{V}_{i,\alpha} dP + RT \ln a_{i,\alpha} + \Psi_{i,\alpha} \quad [2]$$

where $\Psi_{i,\alpha}$ represents potentials generated by other fields. For example, if an electrostatic potential ϕ exists in a given phase, $\Psi_{i,\alpha} = z_i F \phi_\alpha$, where z_i is the charge number of species i and F is the Faraday's constant.

For phase equilibrium between the membrane (M) and fluid (F) phases, $\mu_{i,M} = \mu_{i,F}$. Use of Eq. 2 in this yields in the absence of external fields

$$\ln \frac{a_{i,M}^F}{a_i} = - \left(\frac{\bar{V}_i}{RT} \right) \Pi_S \quad [3]$$

where $a_{i,M}^F$ and a_i represent the activity of free solvent i in the membrane and fluid phase, respectively, \bar{V}_i is the partial molar volume of i , and Π_S is the swelling pressure. For the case of sorption from vapor, this includes pressure terms due to stretching of the polymer matrix as well as that exerted by the curved vapor-liquid interface in the pore of radius r_p ²⁵

$$\Pi_S = \Pi_M + \Pi_\sigma \quad [4]$$

where Π_σ is given by the equation of Young and Laplace

$$\Pi_\sigma = - \frac{2\sigma \cos \theta}{r_p} \quad [5]$$

where σ is vapor-liquid surface tension, θ is the contact angle, r_p is pore radius $r_p = 2\varepsilon_i/S$, S is specific surface area (m^2/cm^3), and ε_i is pore volume fraction occupied by the liquid given as

$$\varepsilon_i = \frac{\lambda_i}{\lambda_i + r} \quad [6]$$

where λ_i is the solvent loading (mol $\text{H}_2\text{O}/\text{mol SO}_3^-$), and r is the ratio of partial molar volume of polymer membrane \bar{V}_M and solvent \bar{V}_i , or $r = \bar{V}_M/\bar{V}_i$. The total number of water molecules per acid site in the polymer λ_i can be classified as:²⁵ (i) those that are strongly, or chemically, bound to the acid site of the polymer, represented by λ_i^C , and (ii) those that are free to physically equilibrate between the polymer and the fluid phase, λ_i^F

$$\lambda_i = \lambda_i^C + \lambda_i^F \quad [7]$$

λ_i^C is determined by the reaction equilibrium condition $\sum_{i=1}^n \nu_{\rho i} \mu_i = 0$, where ρ denotes the elementary reaction.

Activity.—For solvent (i)-polymer membrane (M) systems, the activity of free solvent in the membrane phase $a_{i,M}^F$ is assumed to be given by the Flory-Huggins model,²⁶ derived on the basis of a quasi-crystalline lattice structure

$$\frac{\Delta \mu_{i,M}(m)}{RT} = \ln a_{i,M}^F = \ln \varepsilon_i^F + \left(1 - \frac{1}{r} \right) (1 - \varepsilon_i^F) + \chi (1 - \varepsilon_i^F)^2 \quad [8]$$

where ε_i^F is the volume fraction of free solvent, $\varepsilon_i^F = \lambda_i^F/(\lambda_i + r)$ and χ is the Flory-Huggins polymer-solvent interaction parameter. The first two terms on the right side of Eq. 8 represent the configurational (entropic) contributions, while the third represents the interaction (enthalpic) contribution to mixing.

Swelling pressure and membrane elasticity.—The swelling pressure may be related to network contractile pressure based on the statistical theory of polymer elasticity. Thus, Flory²⁶ assumed that the polymer chain length distribution can be represented by a Gauss-

ian distribution, and that the polymer chains deform affinely, *i.e.*, the change in the dimensions of individual chains is uniform under stress

$$\Pi_M = G \left(\Phi_M^{1/3} - \frac{1}{2} \Phi_M \right) \quad [9]$$

where Φ_M is the volume fraction of polymer given by $\Phi_M = r/(\lambda_i + r)$, and G is the shear modulus of polymer matrix given by the classical theory of polymer elasticity.²⁶

James and Guth²⁷ had earlier developed the so-called Phantom network theory based on the assumptions that the internal energy is not dependent on the volume, and the entropy may be divided into two parts, one associated with the thermal capacity and the other associated with the number of configurations. Then, the swelling pressure is given by

$$\Pi_M = G \Phi_M^{1/3} \quad [10]$$

For chains of 20 monomers or less, Gusler and Cohen's²⁸ non-Gaussian model is superior to the Gaussian distribution model

$$\Pi_M = G \left(\frac{5}{3} \Phi_M^{1/3} - \frac{7}{6} \Phi_M \right) \quad [11]$$

These expressions, however, provide finite osmotic pressures at zero swelling, in apparent agreement with experimental results for some polymers.²⁹ However, in the case of ion-exchange resins, the swelling pressure is experimentally found to be zero in their dry state and is generally proportional to the extent of swelling.³⁰ Thus, Gregor³¹ suggested an empirical Hookean model to represent the experimental data for ion-exchange resins

$$\Pi_M = aV_1 + b \quad [12]$$

where V_1 is the inner volume, *i.e.*, the total external volume of the resin minus the volume of incompressible polymer matrix including the ionic groups, and a and b are fitted constants. Thus, the theoretical models of swelling pressure are not suitable for our purposes.

Recently, Freger³² has developed a model for phase-separated swollen polymer networks by treating the swelling as a non-affine "inflation" of the hydrophobic matrix by small aggregates of water molecules, which is in keeping with the structural model of polymer swelling, resulting in

$$\Pi_M = \frac{2}{3} G (\Phi_M^{1/3} - \Phi_M^{7/3}) \quad [13]$$

Although the application of Eq. 13 is limited to low and moderate swelling, it provides the correct limiting dependence of swelling pressure on the solvent content in ion-exchanged polymers. Among the four models for swelling pressure mentioned, Freger's model is adopted here because it shows a zero swelling pressure in the limit of dry condition.

The shear modulus G is related to Young's modulus E and Poisson's ratio ν by³³

$$E = 2(1 + \nu)G \quad [14]$$

Assuming $\nu = 0.5$ for Nafion, the shear modulus is, thus, one third of Young's modulus.

Chemical equilibrium and hydration sheath.—From the molecular viewpoint, the acid groups of the polymer interact with water molecules via the ion-dipole forces, and a certain number of water molecules, depending upon the level of hydration, become strongly (or chemically) associated with the ionic groups, forming the primary hydration sheath.³⁴ The formation of the hydration sheath was described by us as stepwise equilibrium,²⁵ resulting in the isotherm for the strongly bound molecules as²⁵

Table I. Parameter values employed in the model for the sorption of water in Nafion.

| Parameter | Value | Unit | Comments and references |
|-----------------|---------|---------------------------------|-----------------------------------------------------------------|
| \bar{V}_M | 537 | cm ³ /mol | Partial molar volume of Nafion ²² |
| \bar{V}_i | 18 | cm ³ /mol | Partial molar volume of water |
| S | 210 | m ² /cm ³ | Specific pore surface area ⁴¹ |
| K_1 | 1000 | Dimensionless | The first ionization constant of sulfuric acid ⁴²⁻⁴⁵ |
| ν | 5 | Dimensionless | The number of chemical equilibrium steps of reaction |
| $\lambda_{i,m}$ | 1.8 | Dimensionless | Monolayer coverage being bound ^{22,25} |
| σ | 72.1 | mN/m | Surface tension of water |
| θ | 98 | Dimensionless | Contact angle of saturated water vapor in Nafion ⁴⁶ |
| χ | 0.9-2.4 | Dimensionless | Fitted polymer-solvent interaction parameter |

$$\lambda_i^C = \frac{\sum_{j=1}^{\nu} (\prod_{\rho=1}^{\nu} K_{\rho}) j (a_i)^j}{1 + \sum_{j=1}^{\nu} (\prod_{\rho=1}^{\nu} K_{\rho}) (a_i)^j} \quad [15]$$

where j is the number of strongly bound solvent molecules, K_{ρ} is the equilibrium constants for elementary reaction ρ , and ν is the number of equilibrium steps. It was shown²⁵ that an adequate expression for λ_i^C is

$$\lambda_i^C = \lambda_{i,m} \frac{K_1 a_i}{1 - a_i} \left(\frac{1 - (\nu + 1)(a_i)^{\nu} + \nu(a_i)^{\nu+1}}{1 + (K_1 - 1)a_i - K_1(a_i)^{\nu+1}} \right) \quad [16]$$

The additional parameter $\lambda_{i,m}$ can be estimated from a knowledge of the total number of water molecules in the primary hydration sheath at saturation ($a_i = 1.0$). From Eq. 15

$$\lambda_i^{C,sat} = \lambda_{i,m} \frac{(1 + \nu)}{2[1 + 1/(K_1 \nu)]} \approx \lambda_{i,m} \frac{(1 + \nu)}{2} \quad [17]$$

The sorption of water in Nafion can thus be calculated by the substitution of Eq. 4-8 and 13 into Eq. 3. This results in an implicit expression for λ_i vs. a_i

$$\begin{aligned} & \ln \left(\frac{\lambda_i - \lambda_i^C}{\lambda_i + r} \right) + \left(1 - \frac{1}{r} \right) \left(\frac{\lambda_i^C + r}{\lambda_i + r} \right) + \chi \left(\frac{\lambda_i^C + r}{\lambda_i + r} \right)^2 - \ln a_i \\ & = -\frac{\bar{V}_i}{RT} \left\{ \left[\frac{2}{3} G \left[\left(\frac{r}{\lambda_i + r} \right)^{1/3} - \left(\frac{r}{\lambda_i + r} \right)^{7/3} \right] \right. \right. \\ & \quad \left. \left. - S \sigma \cos \theta \left(1 + \frac{r}{\lambda_i} \right) \right] \right\} \quad [18] \end{aligned}$$

where λ_i^C is provided in Eq. 16 or 17. The isotherm, *i.e.*, the solvent loading λ_i as a function of activity of fluid phase a_i , can thus be obtained in terms of the parameters listed in Table I, all of which are obtained *a priori* except for the Flory-Huggins interaction parameter χ , which is hence the only fitted parameter in this model.

Experiments

Membrane preparation.—Nafion membrane of EW of 960, 1100, and 1200 were prepared by casting the Nafion solution based on the procedure described by Moore and Martin.³⁵ After stirring for 8 h at room temperature, the solution was cast on a glass dish utilizing a doctor blade. The cast membrane was heat-treated in a convection oven at 100°C for 15 min, which was sufficient to produce a solid membrane. The fabricated membrane was removed from the glass dish, dried, and then placed in a Teflon sleeve and annealed at 170°C for 15 min in a mechanical press. This processing step is necessary to produce pliant and insoluble PEMs with mechanical properties similar to those of the commercially available Nafion films.

Water sorption measurement.—The water uptake of Nafion was measured via TEOM³⁶ under different RH conditions. The changes in sample mass are measured in TEOM via the frequency changes of the oscillating tapered element. The membranes were cut into thin strips (1.5 × 1.5 mm) and packed with quartz wool into the oscillating chamber of the TEOM. The water uptake was measured at 25°C from 0 to 99% RH. The lines to the TEOM were heat-traced to avoid condensation. The changes in real-time mass were recorded to determine the sorption amount of water at equilibrium.

Young's modulus measurement.—The Young's modulus of Nafion was measured under different humidity conditions using the OEH technique. The Young's modulus E can be obtained by the relation

$$E = \frac{4\pi^2 f_n^2 L^4 \rho A}{\beta_n^4 I} \quad [19]$$

where f_n is the frequency of the n th mode, β_n is a characteristic coefficient, L is the effective length of the sample, ρ is the density, A is the cross-sectional area of the sample, and I is the moment of inertia of the cross section of the sample. The experimental details are described elsewhere.³⁷

Results and Discussion

The isotherm for water vapor in Nafion is calculated by Eq. 18. The model parameters, *i.e.*, K_1 , $\lambda_{i,m}$, ν , G , and χ , were determined based on the following considerations. The first ionization constant K_1 between water and the side chain of SO₃H is approximated as 10³ based on the report that pK of a Nafion is in the range of -1.0 to -5.1.³⁸ The parameter, $\lambda_{i,m}$, was obtained from Eq. 17 by assuming $\lambda_i^{C,sat} \approx \nu$ along with the assumption that $\nu = 5-6$. This provides $\lambda_{i,m} = 1.8$, which is also approximately the number of water molecules per acid site for monolayer coverage.²⁵ Because the number of water molecules in the first hydration shell around sulfonic acid in Nafion varies from 4 to 6 depending on the type of cations coexisting with the sulfonic acid,^{39,40} the number of the equilibrium steps is in the range of 4-6 for water sorption in Nafion.

Young's modulus of H⁺-Nafion (EW = 1100) at room temperature was measured utilizing the OEH technique described previously and fitted using the empirical formula

$$E = E_0 \exp(-2.1753\varepsilon_i) \quad [20]$$

where $E_0 = 316$ MPa for the dry membrane and ε_i is the volume fraction of water in Nafion. Thus, as the volume fraction of water in the membrane phase increases, the Young's modulus decreases. The Flory-Huggins interaction parameter, χ , is also usually a composition-dependent term and is fitted to experimental data of sorption.

Figure 1 shows the isotherm of water in Nafion (EW = 1100) in terms of λ_i as a function of the activity of water in vapor phase, based on parameters⁴¹⁻⁴⁶ listed in Table I and the fitted composition-

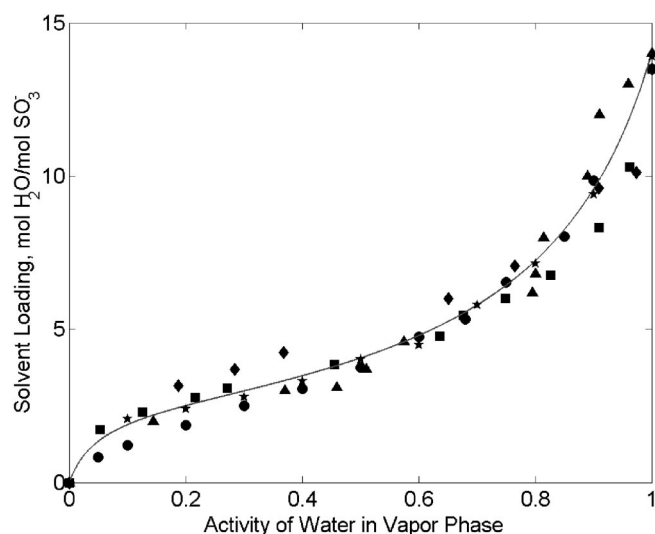


Figure 1. Solvent loading vs. activity of water vapor for Nafion (EW 1100) membrane: (▲) Ref. 47, (■) Ref. 48, (◆) Ref. 49, (●) Ref. 50, and (★) this work.

dependent Flory-Huggins interaction parameter shown in Fig. 2, along with the experimental data from literature.⁴⁷⁻⁵⁰ In the low-activity region, $a_i < 0.75$, water uptake increases only gradually with activity. After the sorption of strongly bound water molecules, the water uptake in this activity region increases with the activity and reaches $\lambda_{i,V} \approx 6$ at $a_{i,V} = 0.75$. For $a_{i,V} > 0.75$, the water uptake is very sensitive to the activity of the water vapor and reaches $\lambda_{i,V}^{\text{sat}} = 14.0$ at saturation. The model reflects well the sorption of water in Nafion with the concentration-dependent interaction parameter χ . In addition, the model predicts the Schroeder's paradox,²⁵ *i.e.*, $\lambda_{i,L}^{\text{sat}} \approx 22.0$ for sorption from liquid water.

Figure 2 shows the dependence of χ on the volume fraction of free water in Nafion. The interaction parameter decreases with the volume fraction of free water in Nafion. This may be explained by the fact that the free water molecules face different environments within the polymer matrix with increasing water imbibition, and thus interaction parameter varies with the water content in Nafion. In fact, the fitted interaction parameter between water and Nafion

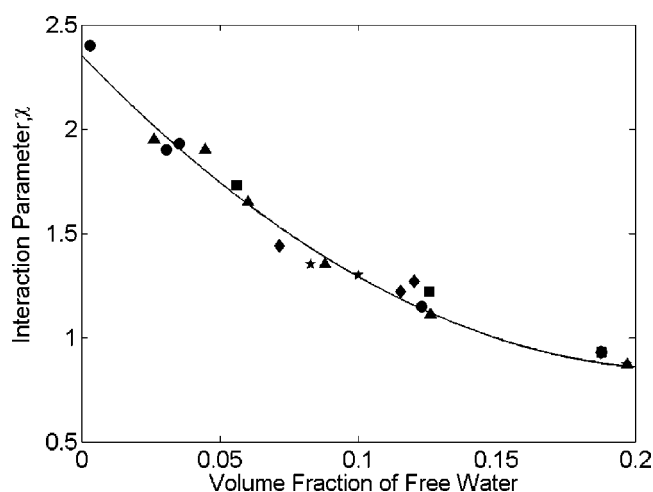


Figure 2. The interaction parameter χ as a function of activity of water vapor: (▲) Ref. 47, (■) Ref. 48, (◆) Ref. 49, (●) Ref. 50, and (★) this work.

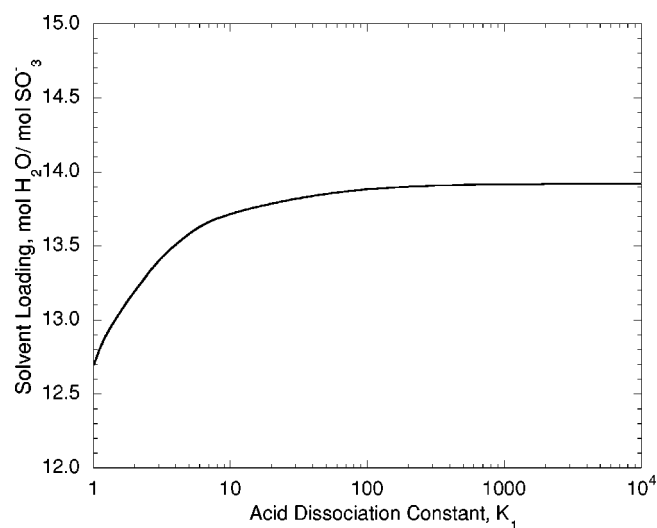


Figure 3. Predicted solvent loading with changes of the dissociation constant.

depends on the type of sorption model and parameter employed. Thus, Tsonos *et al.*²³ considered the volume fraction of water in Nafion based on the total amount of water in Flory-Huggins activity expression and obtained χ increasing with water uptake to an activity of water $a_i = 0.79$ and thereafter decreasing. Futerko and Hsing²⁴ treated the strongly bound water molecules as part of the Nafion and found that χ increases linearly with the free water fraction.

In order to use the sorption model described here for design purposes, the effect of the polymer variables K_1 (acid strength) and E (membrane elasticity) on the amounts of water uptake is analyzed. The pK for Nafion has been suggested to be in the range between that for methane sulfonic acid ($pK = -1.0$)⁴² and tri-fluoro methane sulfonic acid ($pK = -5.1$)⁴³ and has recently been reported to be -3.09 ⁴⁴ and -6.45 .⁴⁵ Figure 3 shows the effect of the dissociation constant K_1 on the water sorption. As the dissociation constant increases, *i.e.*, as pK decreases, the water uptake increases initially and reaches $\lambda_i = 13.9$ at $K_1 = 10^2$ and then no further increase in water uptake is predicted. Thus, there appears to be a limit to the acid strength of acid sites, beyond which the water uptake is not affected by it.

Figure 4 shows the effect of Young's modulus of the polymer in the dry state E_0 on the water uptake. E_0 varies with the polymer type and the temperature. The water uptake increases as expected for polymers having low E_0 . However, this must be balanced by other considerations such as mechanical durability and strength of a membrane in an operating fuel cell.

The number density of the acid groups also strongly affects the sorption capacity of the polymer on a weight or volume basis, even though λ_i may remain unchanged. A high number density of acid groups is characterized by lower EW. The variation of EW strongly affects the crystallinity, elasticity, swelling, and the transport properties of the polymer. Therefore, for a given polymer system, EW is one of the most critical design parameters to be optimized. Figure 5 compares the model predictions vs. experimental results of the water vapor sorption in Nafion with EW 960, 1100, and 1200 g/equiv. As expected, the water uptake in terms of wt % of dry membrane increases with decreasing EW. The total number of water molecules sorbed per acid site, however, remains the same for EW in the range of 960-1200 in the case of vapor sorption, in accordance with the predictions by the model. The water uptake from liquid phase has been reported for different EWs of Nafion. For example, for H^+ -Nafion, water sorption increases with decreasing EW from 1500

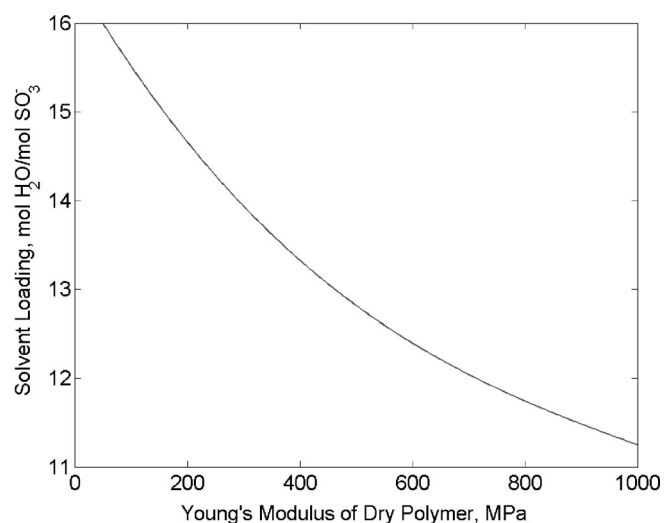


Figure 4. Predicted solvent loading with changes of Young's modulus.

to 785 on a dry weight basis.¹⁸ For EW less than 900, however, the water uptake of Nafion increases dramatically, e.g., the water uptake reaches 80 wt % on a dry Nafion basis at EW of 785. This high water uptake at very low EW can be explained by a substantial decrease of Young's modulus with EW and sorbed amount. However, Freger's model adopted here is limited to low sorption amounts. The membrane becomes soft at this low EW condition and may lose its integrity, forming a gel solution instead.

In summary, the water uptake of PEMs increases with the activity of the functional group (K_1) up to certain extent, low Young's modulus of polymer elasticity (E), and low EW of polymer. Although high water uptake is desirable for high proton conductivity in general, too high a water uptake could lead to an overly swollen state and eventual destruction of the membrane. Therefore, an optimal level of water uptake is needed to maintain the stability of the membrane. This can be realized, in principle, by the appropriate balance of the previous properties.

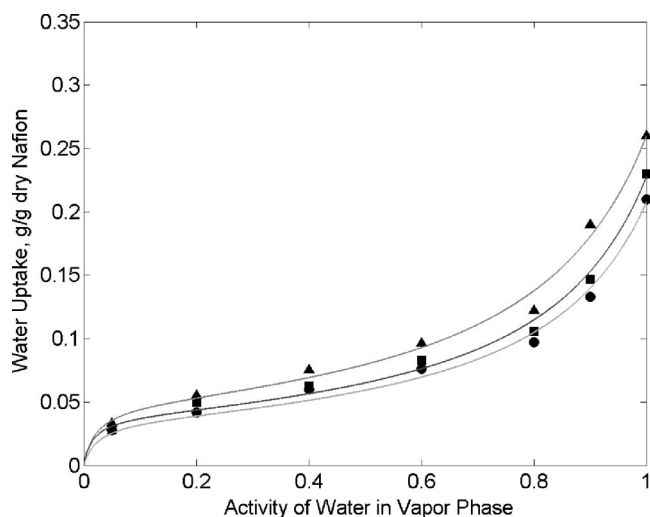


Figure 5. Effect of EW on water vapor sorption for different RH conditions at room temperature: (▲) EW = 960, (■) EW = 1100, and (●) EW = 1200.

Conclusions

A sorption model has been proposed based on the thermodynamic analysis using the Flory-Huggins activity model and Freger's elastic model, and compared to data on sorption from literature and obtained by us using TEOM. The model reflects the sorption equilibrium in PEMs satisfactorily and contains all the important design variables such as dissociation constant of acid groups K_1 , elasticity of polymer matrix represented by Young's modulus E and measured here by OEH, hydrophobicity of polymer surface represented by polymer-solvent interaction χ , and the number of acid groups represented by the polymer EW. For a given polymer system, the sorption amount per unit mass of dry polymer increases with high acid strength, low Young's modulus, and low EW. The thermodynamic sorption model developed here provides a theoretical framework of understanding swelling, sorption, and ion-exchange equilibrium in PEMs. The model also provides helpful indications for developing and comparing alternative PEMs for fuel cell applications.

Worcester Polytechnic Institute assisted in meeting the publication costs of this article.

References

1. P. Costamagna and S. Srinivasan, *J. Power Sources*, **102**, 242 (2001).
2. M. L. Perry and T. F. Fuller, *J. Electrochem. Soc.*, **149**, S59 (2002).
3. V. Mehta and J. S. Cooper, *J. Power Sources*, **114**, 32 (2003).
4. J. Roziere and D. J. Jones, *Annu. Rev. Mater. Sci.*, **33**, 503 (2003).
5. G. Alberti and M. Casciola, *Annu. Rev. Mater. Sci.*, **33**, 129 (2003).
6. M. Rikukawa and K. Sanui, *Prog. Polym. Sci.*, **25**, 1463 (2000).
7. Y. Sone, P. Ekdunge, and D. Simonsson, *J. Electrochem. Soc.*, **143**, 1254 (1996).
8. C. H. Wirguin, *J. Membr. Sci.*, **120**, 1 (1996).
9. T. D. Gierke, Abstract 438, p. 1139, The Electrochemical Society Extended Abstracts, Vol. 77-2, Atlanta, GA, Oct 9-14, 1977.
10. K. A. Mauritz, C. J. Hora, and A. J. Hopfinger, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)*, **19**, 324 (1978).
11. H. L. Yeager and A. Steck, *J. Electrochem. Soc.*, **128**, 1880 (1981).
12. G. Gebel, *Polymer*, **41**, 5829 (2000).
13. H.-G. Haubold, Th. Vad, H. Jungbluth, and P. Hiller, *Electrochim. Acta*, **46**, 1559 (2001).
14. R. S. Mclean, M. Doyle, and B. B. Sauer, *Macromolecules*, **33**, 6541 (2000).
15. J. T. Hinatsu, M. Mizuhata, and H. Takenaka, *J. Electrochem. Soc.*, **141**, 1493 (1994).
16. C. M. Gates and J. Newman, *AIChE J.*, **46**, 2076 (2000).
17. P. D. Beattie, F. P. Orfino, V. I. Basura, K. Zychowska, J. Ding, C. Chuy, J. Schmeisser, and S. Holdcroft, *J. Electroanal. Chem.*, **503**, 45 (2001).
18. M. Doyle, L. Wang, Z. Yang, and S. K. Choi, *J. Electrochem. Soc.*, **150**, D185 (2003).
19. A. Steck and H. L. Yeager, *Anal. Chem.*, **52**, 1215 (1980).
20. D. Nandan, H. Mohan, and R. M. Tyer, *J. Membr. Sci.*, **71**, 69 (1992).
21. T. A. Zawodzinski, T. E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio, and S. Gottesfeld, *J. Electrochem. Soc.*, **140**, 1981 (1993).
22. T. Thampan, S. Malhotra, H. Tang, and R. Datta, *J. Electrochem. Soc.*, **147**, 3242 (2000).
23. C. Tsanos, L. Apekis, and P. Pissis, *J. Mater. Sci.*, **35**, 5957 (2000).
24. P. Futerko and I. M. Hsing, *J. Electrochem. Soc.*, **146**, 2049 (1999).
25. P. Choi and R. Datta, *J. Electrochem. Soc.*, **150**, E601 (2003).
26. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY (1953).
27. H. M. James and E. Guth, *J. Chem. Phys.*, **11**, 455 (1943).
28. G. M. Gusler and Y. Cohen, *Ind. Eng. Chem. Res.*, **33**, 2345 (1994).
29. M. Gottlieb and R. J. Gaylord, *Macromolecules*, **17**, 2024 (1984).
30. G. E. Boyd and B. A. Soldano, *Z. Elektrochem.*, **57**, 162 (1953).
31. H. P. Gregor, *J. Am. Chem. Soc.*, **73**, 642 (1951).
32. V. Freger, *Polymer*, **43**, 71 (2002).
33. E. A. Grulke, *Polymer Process Engineering*, Prentice-Hall, Inc., Englewood Cliff, NJ (1994).
34. J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry 1*, p. 294, Plenum Press, NY (1998).
35. R. B. Moore and C. R. Martin, *Anal. Chem.*, **58**, 2570 (1986).
36. J. E. Resoke and M. A. Barteu, *J. Phys. Chem. B*, **101**, 1113 (1997).
37. S. P. Mizar and R. J. Pryputniewicz, in *Proceeding of the IX International Congress on Experimental Mechanics*, The Society for Experimental Mechanics, Bethel, CT, p. 1013 (2003).
38. R. W. Kopitzke, C. A. Linkous, H. R. Anderson, and G. L. Nelson, *J. Electrochem. Soc.*, **147**, 1677 (2000).
39. S. R. Lowry and K. A. Mauritz, *J. Am. Chem. Soc.*, **102**, 4665 (1980).
40. A. Vishnyakov and A. V. Neimark, *J. Phys. Chem. B*, **104**, 4471 (2000).
41. J. Divisek, M. Eikerling, V. Mazin, H. Schmitz, U. Stimming, and Yu. M. Volkovich, *J. Electrochem. Soc.*, **145**, 2677 (1998).
42. V. Z. P. Stang and V. Zhdankin, in *Chemistry of Organic Fluorine Compounds II*, M. Hudlicky and A. E. Pavlath, Editors, p. 956, American Chemical Society, Washington, DC (1995).

43. B. E. Smart, in *Chemistry of Organic Fluorine Compounds II*, M. Hudlicky and A. E. Pavlath, Editors, p. 988, American Chemical Society, Washington, DC (1995).
44. C. Ma, L. Zhang, S. Mukerjee, D. Ofer, and B. Nair, *J. Membr. Sci.*, **219**, 123 (2003).
45. K. D. Kreuer, *J. Membr. Sci.*, **185**, 29 (2001).
46. T. A. Zawodzinski, S. Gottesfeld, S. Shoichet, and T. J. McCarthy, *J. Appl. Electrochem.*, **23**, 86 (1993).
47. T. A. Zawodzinski, M. Neeman, L. O. Shillerud, and S. Gottesfeld, *J. Phys. Chem.*, **95**, 6040 (1991).
48. D. R. Morris and X. Sun, *J. Appl. Polym. Sci.*, **50**, 1445 (1993).
49. K. K. Pushpa, D. Nandan, and R. M. Iyer, *J. Chem. Soc., Faraday Trans. 1*, **84**, 2047 (1988).
50. D. Rivin, C. E. Kendrick, P. W. Goibson, and N. S. Schneider, *Polymer*, **42**, 623 (2001).